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(54) **Fluorescent compounds.**

(57) Novel compounds obtainable by reacting together an imido-reagent such as diphenylphosphonimido-triphenylphosphorane) with a chelate of a transition or lanthanide or actinide metal, such as tris(dibenzoylmethide) europium III, has the property of fluorescing in UV radiation. The invention includes solid polymer bodies containing such compounds, or chelates of transition or lanthanide or actinide metals generally, the bodies having the property of emitting light by virtue of internally generated, e.g. by tritium ionising radiation. The body is preferably of polystyrene formed by polymerising the monomer in the presence of the compound or metal chelate.

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This invention concerns polymer bodies which are light-emitting by virtue of containing a transition or lanthanide or actinide metal chelate or other complex. For the most part, the energy for light emission is provided by internal radioactivity, e.g. by using a tritiated polymer. In the course of the work leading to this invention, novel compounds based on certain metal chelates have been identified as having outstanding fluorescent properties. These compounds, and polymer bodies containing them, also form part of this invention. All these compounds and chelates are fluorescent, in the sense that they emit light or other relatively long wavelength electromagnetic radiation, on being subjected to UV or other relatively short wavelength electromagnetic radiation, including ionising radiation from radioactive decay. It is surprising that the compounds and chelates show high efficiency of light output and good stability in the presence of ionising radiation.

British patent specification 2242908 describes tritiated light emitting polymer compositions, containing one or more organic fluors linked to the polymer in some way, for example as a result of having been dissolved in the monomer prior to polymerisation. The polymer compositions can be made transparent or translucent so that useful light is emitted from the entire volume of the polymer. Such compositions have other advantages: they are easily fabricated and shaped; the tritium is present in combined form and so is not released by accidental damage (as would for example be the case with a glass envelope containing gaseous tritium); when performance falls off, the composition is easily replaced and recycled. But using the organic fluors described, the generation of light from radioactive decay is not as efficient as may be desired. As a result, the polymer composition may be subject to radiation damage from the high concentrations of tritium needed to generate bright light.

Rare earth chelates having the property of fluorescing in UV radiation are well known. A. P. B. Sinha (Spectroscopy in Inorganic Chemistry edited by C. N. R. Rao and John R. Ferraro, Vol. 2, Academic Press 1971 - History of Congress Catalogue No. 77-117102) describes several classes of rare earth chelates with various monodentate and bidentate ligands. The mechanism of fluorescence is also described. The first step involves the absorption of energy by the organic part of the chelate leading to its excitation from a ground state singlet to an excited singlet. The excited molecule can then go over to a triplet state in which energy can be transferred to a central rare earth metal ion. The excited metal ion can then undergo a radiative transition resulting in the characteristic line emission of the ion (ion fluorescence). All these steps take place in competition with other non-radiative steps. For efficient fluorescence, it is necessary that the transition metal ion have a resonant frequency which is close to, but slightly lower than, the excited triplet frequency of the chelating group. This ensures that the probability of triplet-to-resonance level transition is high. Other complexes of Group IIIA metals and rare earth and lanthanide metals with aromatic complexing agents have been described by G. Kallistratos (Chimika Chronika, New Series, 11, 249-266, 1982). For example, this reference describes the Eu 3+, Tb 3+ and U 3+ complexes of diphenyl-phosphonimido-triphenyl-phosphoran.

In one aspect this invention provides a solid body comprising an organic polymer or a mixture of organic and inorganic polymer, together with a chelate of a transition or lanthanide or actinide metal, the body having the property of emitting light by virtue of internally generated ionising radiation. Preferably the polymer is radioactively labelled so that the radioactive decay provides the ionising radiation.

The metal chelate may be the same as or similar to the known classes of metal chelate referred to above. However, it needs to have a number of special properties not always possessed by the known fluorescers:

- It needs to be capable of fluorescing under the impact of UV or other electromagnetic radiation, not only in pure form but also in dispersion or solution in an organic monomer or polymer.
- It is preferably soluble in the monomer or monomer mix used to form the polymer body. A solubility of at least 10% by weight is generally preferred. The metal chelate should preferably remain soluble as the monomer polymerises.
- The presence of the metal chelate should preferably not inhibit polymerisation of the monomer to a transparent wholly or substantially colourless polymer.

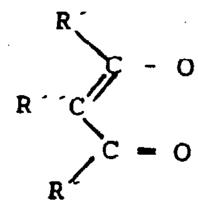
Up to the present time a scintillant has normally been regarded as consisting of a solvent plus one, two or three solutes. The solute with the fluorescence level highest in energy is called the primary solute or scintillator and the second and third solutes are known and act as wavelength shifters. The scintillation process has thus been seen as involving the following steps: absorption of nuclear radiation by the solvent with the formation of a solvent excited state; energy transfer from the solvent to a primary scintillant followed by fluorescence emission; absorption and re-emission by secondary and possibly tertiary scintillants to shift the final emitted light to the desired wave-length.

It has surprisingly been discovered that the chelates of the transition metals particularly those of the rare earths, can act as primary scintillants, such that the nuclear radiation energy adsorbed by the solvent (polymer) is transferred to the chelate or chelates and only emitted at the final desired wavelength, this process being achieved without the use of secondary or tertiary scintillants or wave-shifters. These chelates have thus minimised energy losses and give rise to more efficient light output. The metal chelates often have very narrow

emission spectral bands, which can be designed to be at particular wavelengths, thus enabling photodiodes to be used at high efficiency.

In principle, any metal ion having an unfilled inner electron shell, that is to say almost any transition or lanthanide or actinide metal ion, can be used as the basis of the fluorescent chelate. In practice, a metal ion having a convenient emission frequency, and a convenient resonant frequency, and an efficient transition between the two, is most usually chosen. The most usual are the lanthanide metal ions Sm 3+, Eu 3+, Tb 3+, Dy 3+, Yb 3+, Lu 3+, Gd 2+, Eu 2+, and the actinide metal ions U 3+ and UO_2 3+.

The chelating or complexing groups are chosen to have a triplet energy level similar to but slightly higher than the resonant energy level of the chosen metal ion. Known chelates, including those described in the abovementioned references are likely to be suitable, including those based on diketone and triketone chelating moieties. A preferred chelating group has the formula



where R' may be the same or different at different parts of the molecule and each R" and R' is an aromatic or heterocyclic ring structure which may be substituted or hydrocarbon or fluorocarbon or R" is hydrogen. The identity of R" can be used to modify the triplet energy and may affect light emission. R" can also be made co-polymerisable with a monomer, e.g. styrene.

In the compound described in Example a) below, R' is t-butyl and R" is hydrogen. Metal chelates may have up to four, typically three, of such groups surrounding the metal ion.

Examples of metal chelates useful in this invention are:-

a) Terbium (3+) (dipivaloylmethide)$_3$, otherwise known as terbium tris(2,2,6,6-tetramethyl-3,5-heptanedionato) chelate, commercially available from Strem Chemicals.

b) The di- and tri-pyrazolyl borate and the di- and tri-pyrazolyl-N-oxide borate adducts of a).

c) Europium (3+) (2-naphthyl trifluoroacetyl acetonate)$_4$

d) Uranyl (2-naphthyl trifluoroacetyl acetonate)$_4$. This material emits strongly in the yellow part of the spectrum when cooled to about -50°C.

e) The dipyridyl and dipyridyl-N-oxide adducts of c) and d).

f) A family of novel compounds derived from metal chelates as in a) to e) above has shown interesting fluorescent properties and is included within the scope of the invention.

In this aspect the invention provides a compound that results from reacting together an imido-reactant of formula

$$\begin{array}{c} \quad R \\ \quad | \\ O = Q - N = Z \\ \quad | \\ \quad R \end{array}$$

where Q may the same or different at different parts of the molecule and is P, As or Sb,

and R may be the same or different at different parts of the molecule and each R is an aromatic or heterocyclic ring structure which may be substituted or unsubstituted, provided that one group R may alternatively be a co-polymerisable group,

and Z is either QR_3 or an oligophosphoranyl group (an organophosphoranyl group with two or more P atoms),

with a chelate of a transition or lanthanide or actinide metal ion to produce a product which has the property of fluorescing in UV radiation.

These compounds are expected to have the formula

$$(X_n - M - O - QR_2 - N)_p Z \text{ or } X_n - M(-O-QR_2-N=Z)_n$$

where M is the transition or lanthanide or actinide metal ion, such as those described above,
X is a chelating group,
n is 1 to 4,
p is 1 to 4, and
s is 1 to 4 preferably 1 or 2.

In the above structures, Q may be Sb or As or P, the latter being preferred. At least four of the five groups R should be of aromatic or heterocyclic character, the following being examples: phenyl; p-tolyl; 2,4-dimethylphenyl; p-tertiary butyl phenyl; 1-naphthyl; 2-naphthyl; 4-pyridyl; 4-quinolyl.

Z may be an oligophosphoranyl group, e.g. of the formula:

$$Ar_1 - P - [(Alk - P - Ar)_m - Alk - P - Ar_2]_q$$

where Ar is aryl preferably phenyl,
Alk is alkene preferably $-C_2H_4-$,
1, m and q are small integers such that 1 + q is 3,
these compounds being of the kind commercially available as:-
Diphos - $Ph_2PC_2H_4PPh_2$.
Triphos - $Ph_2PC_2H_4P(Ph)C_2H_4PPh_2$.
Tetraphos I - $Ph_2PC_2H_4P(Ph)C_2H_4PPhC_2H_4PPh_2$.
Tetraphos II - $P(C_2H_4PPh_2)_3$.

(See JACS 93:17 August 25 1971; 4158-4166). For example, a compound according to the invention based on Diphos would have the formula:

$$X_n - M - O - P(Ph)_2 - N = P(Ph)_2 - C_2H_4 - P(Ph)_2 = N - P(Ph)_2 - O - M - X_n$$

where Ph is phenyl.

Alternatively, one of the groups R may be a co-polymerisable group, that is to say a group capable of joining in a polymerisation reaction with a monomer with which the compound is mixed. Examples are carboxylic and sulphonic acid groups, and ethylenically unsaturated hydrocarbon groups such as allyl and p-styryl. A preferred imido reagent has the formula

$$\begin{array}{ccccccccc} & & Ph & & & & Ph & & \\ & & | & & & & | & & \\ O & = & P & - & N & = & P & - & Ph \\ & & | & & & & | & & \\ & & Ph & & & & Ph & & \end{array}$$

where Ph is phenyl.

Preparation of the compounds of this invention is straightforward. Transition metal chelates such as those described by A. P. B. Sinha (reference above) are well known. Some are commercially available. General methods of preparation are described by Reid and Calvin (Journal of the American Chemical Society, 72 (1950), 2948-2952). Imido reagents are known materials (see the Kallistratos reference above) whose preparation is described by R. A. Baldwin and R. M. Washburn (Journal of the American Chemical Society, 83, pages 4466-4467, 1961) and M. J. P. Harger and S. Westlake (Tetrahedron, 38, No. 10, pages 1511-1515, 1982). To prepare compounds according to the present invention, the chosen metal chelate and the chosen imido-reactant may be heated together in molar quantities defined by the formulae above at a melting temperature of 200°C for one hour. More preferably, appropriate molar quantities of the two reactants are heated together in a refluxing organic solvent. The inventors have found trimethylpentane when s is 1 and toluene when s is 2 to be convenient. If the starting metal chelate is insoluble, progress of the reaction can be monitored by noting that the refluxing solution clears. On cooling, the desired product crystallises out in easily recoverable form.

This aspect of the invention is not restricted to compounds prepared by this route, and other preparative methods are possible. For example, one molar part of a complex of the metal ion with the imido-reactant may be heated with generally 2-4 molar parts of the chelating moiety so as to form the desired compound.

The compounds, individually, have the property of fluorescing, in the visible or infra-red region depending on the metal ion chosen, when subjected to UV or other energetic radiation. This property may be exploited in various ways. For example, the compound may be applied as a coating on a glass vessel or on glass beads, and these may be maintained in the presence of a radioactive gas such as tritium or xenon-133 or krypton-85.

The compounds, in combination, may act in a less well known manner. In certain circumstances the energy collected by the metal ion of one structure will not be emitted by that ion but will be transferred most efficiently, by so-called radiationless transfer, to a second different metal ion (chelated). This phenomenon, known as - ion to ion transfer- can be made very efficient by careful selection of the two metal ion structures. For example, trivalent gadolinium structures do not usually emit light even in isolation but, in combination with known fluorescent lanthanide chelates, they prove to be very efficient energy collectors. Such metal ion chelate pairs can be of greater efficiency than any one chelate on its own.

The compounds of this invention are particularly useful in polymer compositions. Thus in another aspect the invention provides a solid body comprising an organic polymer or a mixture of organic and inorganic polymer together with at least one compound as described above, the body being capable of emitting light when subjected to a flux of electromagnetic radiation. Preferably, the flux of electromagnetic radiation is generated internally by radioactivity in the solid body.

Thus, either the polymer or the metal chelate (which term is hereafter used to include novel compounds of this invention) may be radio-labelled, preferably with tritium. In these compositions, the metal chelates act as scintillants, either alone or in conjunction with conventional organic scintillants.

Polymers labelled with tritium are well known, and are most conveniently prepared by labelling a monomer or co-monomer with tritium prior to polymerisation. The polymer should preferably be clear for maximum efficiency at the wavelength of the emitted light, and should preferably be resistant to damage by self-irradiation (E.A. Evans, Tritium arid its Compounds, 2nd Edition, Butterworths, London 1974 pages 720-721). On these grounds, polymers of vinyl-aromatic hydrocarbons, such as styrene and vinyltoluene, are preferred. A G_8 (scission) value of 0.04 is quoted for irradiation of polymethylstyrene and a G_x (cross-linking) value of 0.02 which is much less than for other known polymers, see Polymer Photophysics and Photochemistry by J. Guillet Pub. Cambridge University Press, 1985 page 353 et seq. Some or all of the protium hydrogen in the polymer and/or in the metal chelate may be replaced by deuterium. Additional stability is however conferred on the composition by the presence of the metal chelates, by virtue of their conversion of beta radiation energy into light, reducing the proportion of energy available for self-irradiation of the polymer.

The extent of tritium labelling is a compromise between several factors. By incorporating 2 atoms of tritium per monomer molecule, it is possible to achieve activities of 600 Ci/g. Such monomers may be diluted with non-radioactive monomer, or the monomer prepared using tritium-hydrogen mixtures in the tritiation/hydrogenation step, to achieve the overall specific radioactivity required. Activities below about 100 mCi/g are rather unlikely to be useful as illuminating devices but do have a use as light sources for calibration. As the tritium labelled polymer is a relatively expensive material, it will generally be preferred to use the minimum required to achieve the desired light output. All polymers labelled with radioisotopes including polystyrene suffer from radiation damage, and at high levels of activity this may lead to darkening with loss of light output, and eventually to embrittlement and degradation. Labelling to an activity of from 25 nanocuries/gram to 100 Ci/g, particularly 50 nanocuries/gram to 5 curies/gram, of composition may be appropriate in many cases, with activities towards the lower end of that range where a service life of more than five years is required.

Tritiated vinyl aromatic monomers may be made by the catalytic partial reduction by tritium of substituted acetylenes. For the purpose of this invention, reduction is carried out with tritium-hydrogen or tritium-deuterium mixtures up to 100 per cent isotopic abundance of tritium as required, preferably in the presence of a platinum or palladium catalyst or other suitable hydrogenation catalyst. The catalyst chosen should not contain volatile components such as quinoline and should not be adversely affected by monomer stabilisers. After the reduction it is preferable to remove by filtration or by distillation any catalyst from the tritiated monomer. It is also preferable to dilute the tritiated monomer with non-radioactive monomer(s) which have been purified either by distillation or by passage through a column of neutral alumina. Vinyl aromatic monomers which are tritium labelled on the aromatic ring are also known and may be used.

The concentration of the metal chelate should be enough to efficiently convert the beta-radiation into visible light, but not so great as to inhibit polymerisation of the monomer mix or to substantially harm the properties of the polymer. While optimum concentrations may vary depending on the nature of the polymer, the extent of tritium labelling, and the nature of the scintillant, suitable concentrations are likely to lie in the range 1 μg to 500 mg, preferably 10 - 200 mg of total scintillant per ml of polymer. The concentration of scintillants are optimised for the light output required but too high a concentration will result in self-absorption of the light and thus reduce the efficiency - see Design Principles of Fluoresence Radiation Converters by G. Keil in Nuclear Instruments and Methods 87, 111-123 (1970).

A cross-linking agent may be included in the monomer mix and may be beneficial in increasing light output, as discussed below. For example, with a vinyl aromatic system, up to 50 g/l of divinylbenzene may be useful.

These light-emitting polymer compositions may be made by providing a reaction mix comprising at least one polymerisable organic monomer, preferably a vinyl-aromatic hydrocarbon, labelled with tritium, and at least

one metal chelate scintillant,and subjecting the reaction mix to polymerisation conditions. The scintillant is preferably present in solution in the monomer. Transition metal chelates are often sparingly soluble in vinyl-aromatic monomers; a preferred feature of adducts such as the aromatic imido-moiety is to render the compounds of this invention highly soluble. Preferably, polymerisation of the monomer or monomers is effected by heat in the presence or absence of free-radical polymerisation initiators and in the substantial absence of oxygen. When the polymerisation reaction is exothermic, careful temperature control of the reaction mix may be needed to avoid thermal decomposition of the organic scintillators. The reaction mix may be shaped prior to polymerisation to generate plastic sheets of desired thickness, rods, filaments, microbeads, capillary tubing, or other desired shapes. After polymerisation, the solid products can also be cut and shaped as desired. These shapes may be "silvered" in known manner to increase directional light output. Thus the body may be in the shape of cylinder with the curved surface made internally reflecting, or of a chord of a cylinder with the curved surface and the ends made internally reflecting.

Upon polymerisation of the monomer mix, the light emitted by the composition increases, to an extent that is dependent on various factors. Use of purer reagents; increasing the hardness and/or rigidity of the product (and for this reason a cross-linking agent may be beneficial); cooling the product, stretching the product or otherwise inducing crystallisation; all these steps may increase light output from a given composition.

The light emitting compositions of this invention are useful wherever a continuous or intermittent independent light source is required and power lines or batteries cannot conveniently be provided, or as a detector of radiation. Some examples are:

- Production of electricity by combination with photocells.
- In liquid scintillation compositions as well as polymers, e.g. for liquid scintillation beta measurements.
- In radiation, e.g. X-ray, visualisation screens where the efficiency of the new phosphors may be used to reduce exposure and/or improve definition.
- Light sources for signs, gun-sights, markers on instruments.
- Large light sources on airfields and other situations where remote lighting may be required (see also G. Foldiak in Industrial Application of Radioisotopes, Pub. Elsevier 1986, p.386 et seq. and A Novel Light-Collection System for Segmented Scintillation-Counter Calorimeters, V. Eckardt, R. Kalbach, A. Manz, K. P. Pretzl, N. Schmitz and D. Vranic, Nuclear Instruments and Methods, 155, 389-398 (1978).

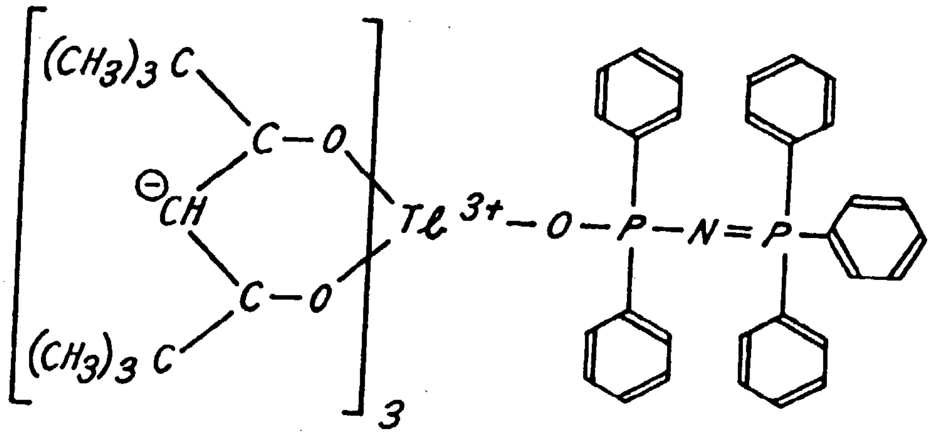
Reference is directed to the accompanying drawings in which:

- Figure 1 is a structure, obtained by X-ray crystallography, of the compound tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium III-diphenyl-phosphonimido-triphenyl phosphorane.
- Figures 2 and 3 are graphs of power output against phosphor concentration at two different polymer tritium concentrations.
- Figure 4 is a graph of light emission intensity against wavelength for different light emitting sources.
- Figure 5 is a graph of power output against radioactive concentration.
- Figure 6 is a graph of light emission intensity against wavelength for the formulations of Example 5.
- Figure 7 is a graph comparing efficiencies in terms of power output, of various light emitting sources.
- Figure 8 is a graph comparing efficiencies, in terms of brightness, of the same light emitting sources.

The following examples illustrate the invention.

EXAMPLE 1

Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium III-diphenyl-phosphonimido-triphenyl phosphorane (ALP-1)



Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium III+ (2) was purchased from Strem Chemicals Inc.

Diphenyl-phosphonimido-triphenyl phosphorane (3) was prepared by a method given in the references quoted above. Diphenyl-phosphinic acid chloride (68 g) and sodium azide (30 g) were stirred in dried acetonitrile (380 ml) for 64 hours. Diphenylphosphinic azide precipitated out of solution, was filtered off and washed with acetonitrile and dried to yield 72.3 g.

24.1 g (100 mM of the diphenylphosphinic azide was dissolved in dry diethyl ether (50 ml) to yield 70 ml solution. Triphenylphosphine (26 g 100 mM) was dissolved in diethyl ether (dried 160 ml) and the two reagents mixed and refluxed in a 500 ml flask fitted with a reflux condenser.

The precipitated material was filtered off, washed with a) ether, b) dilute ammonia solution (10 ml of 2N ammonia diluted to 100 ml), and c) water (5 x 100 ml), and dried at room temperature under vacuum to yield 36.31g (76% of theory) of (3).

1 mM of (2) was mixed with 1 mM of (3) in a total of 5 ml trimethyl pentane, and the mixture heated to reflux until a clear solution was obtained (about 1 hour). The solution was allowed to cool yielding (ALP-1) as a crystalline solid in nearly quantitative yield.

X-ray crystallographic examination of single crystals of the product gave rise to the structure shown in Figure 1. Thermal analysis by differential scanning calorimeter gave a melting point of 169.8°C.

EXAMPLE 2

Light emitting polymer preparation using (1)

Reduction of intermediate to yield diluted tritiated monomer

Phenylacetylene (1 mM 100 mg) was reduced with 60 curies tritium gas in the presence of Pdc catalyst - (reference see Example 5, 1 ml solution pumped to dryness under vacuum) then styrene (10 ml without the stabiliser removed) added along with a magnetic stirrer. The phenylacetylene was quantitatively reduced to tritiated styrene without there being any significant further reduction of the styrene to ethyl benzene.

This produced about 10 millilitres or grams of tritiated styrene at 6 curies/gram or millilitre - still containing Pdc catalyst and polymerisation inhibitor. The tritiated styrene was removed from the catalyst, polymerisation inhibitor and any other contaminants by vacuum distillation and the resulting pure tritiated styrene added as required to (ALP-1) undiluted or diluted to give a final solution of (ALP-1) in the tritiated monomer.

Polymerisation to yield L.E.P.

A solution of polymerisation catalyst (AZBN) was added to yield a final catalyst concentration of 0.1 milligrams per millilitre. The solution was then flushed with argon/methane to minimise oxygen content which tends

to quench light emission, and the container was sealed and the solution polymerised at 60°C for 16 hours.

The polymer was allowed to cool to room temperature to yield a virtually colourless high clarity polymer with a bright yellow/green (545 nanometers) light emission.

A considerable increase in light output was observed as the monomer polymerised to completion.

Polymer shaping and applying reflective coatings

The product may then be further shaped as it is a thermoplastic to emit its light optimally in one plane and further efficiency of emission may be obtained by applying a reflective metal coating to parts of the shaped product. For the tests described below, the body was formed in the shape of a chord of a cylinder with the curved surface and the ends made internally reflecting by being coated with aluminium metal.

Figure 2 is a graph of power output (expressed in nW/Ci) against phosphor concentration at a fixed polymer tritium concentration of 6.06 Ci/g. The upper curve of the graph was obtained in an experiment in which the light emitting body was "silvered" and optically linked to a photodiode. The lower graph was obtained in an experiment in which these steps were omitted.

Figure 3 is a corresponding graph, in which the polymer tritium concentration was 0.606 Ci/g.

Figure 4 is a graph of emitted light intensity against wavelength for compositions having a polymer tritium concentration of 6.06 Ci/g and various phosphor concentrations. Curves 1, 2, 3 and 4 were obtained with different concentrations of phosphor. Curves 5, 6 and 7 are included for comparison, and were obtained using a commercially obtainable source containing tritium gas in a glass vessel coated with zinc sulphide scintillant. The fluorescent emission of the phosphor of this invention is strikingly monochromatic at 545 nm, and the peak intensity at this wavelength is much higher than obtainable from the commercially available sources.

EXAMPLE 3

Preparation of Europium (3+) tetra (naphthalene trifluoroacetylacetonate) bipyridyl ($Eu(NTFA)_4$ bipyr)

Naphthalene trifluoroacetylacetonate (ex Lambda Probes & Diagnostics (Austria). 4.7 millimoles (1.25 grams) were dissolved in ethanol (10 ml) and Europium trichloride (1.04 millimoles, 1.04 grams) dissolved in ethanol (5 ml) was added. The combined solutions were heated at 65°C for 30 minutes.

Bipyridyl (2 millimoles, 352 milligrams) dissolved in ethanol (5 ml) was then added and the solution maintained at 65°C for 30 minutes.

The total volume was then reduced to 10 millilitres, neutralised with sodium hydroxide solution and stored overnight at +2°C.

The resultant precipitate was filtered off, washed with ethanol:water (7:3) (5 ml) and dried at 100°C under vacuum.

EXAMPLE 4

Terbium (3+) (2,2,6,6-tetramethyl-3,5-heptanedionato) chelate was purchased from Strem Chemicals. Methods of preparing the pyrazolyl borates are described by E. Trofimenko J.A.C.S. 89: 13/ June 21 1967. The tri-pyrazolyl borate adduct was prepared by heating stoichiometric amounts of the chelate and the pyrazolyl borate in acetone to dissolution, driving off the acetone and melting the residue to a clear melt at minimum temperature. After cooling, the solid was crushed to a powder and any residual solvent pumped off under vacuum at room temperature.

EXAMPLE 5

Formulations using lanthanide chelates to produce a light emitting polymer emitting at 614 mμ or 548 mμ

Phenylacetylene (3 mmoles, 290 μl) dissolved in styrene - d_8 (5 ml) were added to the dried homogeneous Pdc catalyst obtained from 4 ml of catalyst solution (Brunet + Caubert, J. Org. Chem., 1984, 49, 4058-4060).

The above solution was stirred with 200 curies tritium gas. The phenylacetylene is quantitatively reduced to tritiated styrene without there being any significant further reduction of the styrene to ethyl benzene.

This tritiated styrene dissolved in the fully deuterated styrene - d_8 is removed from the catalyst, polymerisation inhibitor and other contaminants by vacuum distillation.

1 ml aliquots of this material were added to the following:-

a)

Terbium $[DPM]_3$ $P_{\emptyset 3}B$ (see Example 4)		21.1 mg
Butyl PBD (primary scintillant)		100 mg
Divinyl benzene (cross-linker)		10 microlitres
AZBN catalyst for polymerisation		1 mg
	- 1.5 curies	

b)

Terbium $[DPM]_3$ $P_{\emptyset 3}B]$ (different batch to a)		20 mg
Divinyl benzene		20 microlitres
AZBN		1 mg
	- 8.0 curies	

c)

Europium NTFA bipyridyl (see Example 3)		20 mg
Butyl PBD		100 mg
Divinyl benzene		20 microlitres
Triphenyl styryl lead		5 mg
	- 8.0 curies	

The volume of each aliquot was about 1.1 ml. The tritium activity was as stated, achieved by use of different specific activity tritium gas.

All three solutions were sealed under nitrogen, the containers sealed and the solutions polymerised at 60°C for 16 hours.

The polymer was allowed to cool to room temperature to yield clear polymer pieces.

The emission of each piece was measured after shaping to a uniform size and shape in a mould and partially silvering by vapour deposition to guide the light out of one surface.

The emission spectra (see Figure 6), shows that the europium chelate containing polymer piece emits light at ≈ 614 millimicron (orange-red) and the terbium chelates at ≈ 548 millimicrons (yellow-green).

Figure 5 is a graph of power output at 540 nm (expressed in nW) against radioactive concentration (Ci/g) of the polymer. The phosphor concentration was held constant at 120 mg/ml. The power output goes up more or less linearly with increasing radioactive polymer concentration. At the higher concentrations shown, the polystyrene would have had a limited life due to radiation damage.

EXAMPLE 6

Figure 7 is a graph comparing efficiencies of various different light emitting sources, expressed as power output (nW) against polymer radioactive concentration (Ci/g). In this graph:-

Squares (line A) represent polymer sources as described in GB 2242908A.

Erect triangles (line B) represent the formulation of Example 5b).

Inverted triangles (line C) represent formulations according to Example 2 containing a phosphor concentration of 120 - 150 mg/ml of polymer

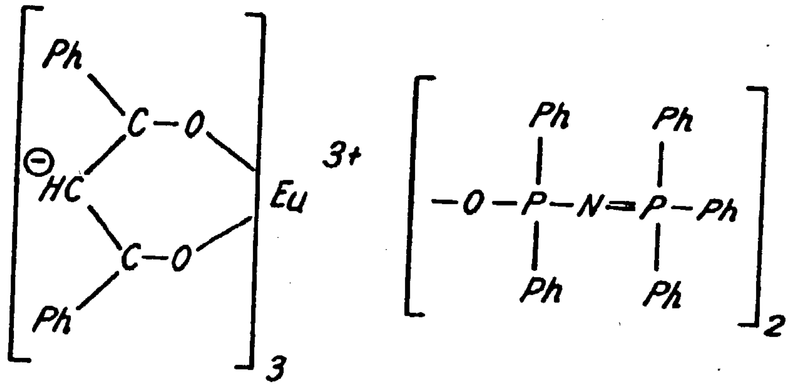
The diamond represents a commercially available source comprising tritium gas contained in a glass vessel coated with a zinc sulphide scintillant.

Figure 8 is a comparable graph, in which the ordinate is not power output but brightness expressed in nW/cm^2 of photodiode. Performance of the Example 5b) formulation (B) is strikingly superior to that of the previously known polymer sources (A). Performance of the formulations (C) according to Example 2 is strikingly superior to the performance of all other sources including the commercially available gas source.

EXAMPLE 7

Tris(dibenzoylmethide)bis(diphenyl-phosphonimido-triphenyl phosphorane) europium III (EuIII[DBM]$_3$-[DPTP]$_2$

A. Preparation of europium III tris(dibenzoylmethide) (EuIII[DBM]$_3$



Dibenzoyl methane, 100 mmoles, 22.43 grams, (ex Aldrich Chemical Co. Ltd.), m.p. 77.5-79°C), and sodium hydroxide 100 mmoles, 4 grams, were reacted together in 50% v/v ethanol:water, 200 ml at room temperature to give a solution of the sodium salt of dibenzoyl methide at a concentration of 0.5 millimoles/ml.

Europium III chloride hexahydrate m.wt. 366.31, 6 millimoles 2.2 grams (ex Aldrich Chemical Co.), was dissolved in 50 ml 50% v/v ethanol:water at c.60°C, and to this was added with stirring 18 millimoles, 36 ml of the solution of sodium dibenzoyl methide prepared as above.

The EuIII[DBM]$_3$ monohydrate precipitates out, is filtered off, washed with water and dried.

B. Preparation of (EuIII[DBM]$_3$[DPTP]$_2$)

EuIII[DBM]$_3$ monohydrate m.wt. 839.74, 2 millimoles, 1.68 grams and diphenyl-phosphonimido-triphenyl phosphorane m.wt. 477.45, 4 millimoles, 1.91 grams are melted together at 200°C in an oven and held at that temperature for one hour. The product is then dissolved in hot toluene 15 millilitres and added carefully to cold stirred trimethyl pentane, 500 millilitres, to precipitate the complex which is filtered off, dried and weighed, yield 3.1 grams, 86% of theory of 3.59 grams, m.wt. 1776.64.

C. Comparison of fluorescent properties of europium III tris(dibenzoyl methide) and its bis(diphenyl phosphonimido-triphenyl phosphorane) derivative prepared as above and incorporated into polystyrene

EuIII[DBM]$_3$, 30 mg was dissolved in 1 ml styrene, polymerised using 1.25 mg AZBN, heating overnight at 75°C, and shaped into a flat sheet ≈1.5 mm thick. Surface reflectance measurements were made at room temperature and at approx. -140°C using an excitation wavelength of 360 nm. EuIII[DBM]$_3$[DPTP]$_2$ 25 mg was similarly treated and measured.

The measurements showed that, without any adjustment for concentration, the fluorescence from EuIII[DBM]$_3$[DPTP]$_2$ in polystyrene was approximately 6.66 times more intense than that of EuIII[DBM]$_3$.

If allowance were to be made for molar concentration then the ratio was 17.29.

The comparisons of the emissions at room temperature and approx. -140°C of the same sample is thought to compare the size of the energy population of the triplet level (measurement at -140°C) with the size of the fluorescence emission (at RT) thereby indicating the efficiency with which that energy has been transferred to the lanthanide ion and emitted. On this basis:

EuIII[DBM]$_3$ shows an efficiency of 36%.

EuIII[DBM]$_3$[DPTP]$_2$ shows an efficiency of 79.72%. i.e. a 2.2 fold increase in efficiency.

The corresponding Samarium III chelates, namely SmIII[DBM]$_3$[DPTP]$_2$ and SmIII[DBM]$_3$[DPTP] have also been made and tested; the former of these two shows good fluorescence properties, the latter also fluoresces in polystyrene.

EXAMPLE 8

Various analogues of styrene were investigated as potential light emitting polymer matrices.

The monomers were polymerised (as described in Example 2) with a fixed amount of compound (1) (Example 1) hereinafter called ALP-1 at fixed radioactive concentration. The radioactivity was introduced by 'spiking' the monomer with small quantities of tritiated styrene (<10% v/v). The results are shown in Table 1.

Table 1. Relative light Output of Some Styrene Analogues

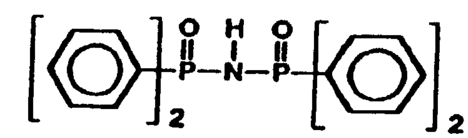
Styrene Analogue	Relative Light Outputs (Arbitrary Units)
Styrene	100
4-t-Butylstyrene	106
4-Methylstyrene	97
2,4-Dimethylstyrene	88
4-Methoxystyrene	60
2,4,6-Trimethylstyrene	39
4-Vinyl-biphenyl	65

Polymerisations carried out at 100°C. t-butyl peroxide initiator (1.5% w/v), 10% ALP w/v.

EXAMPLE 9

Some 1,3-diketonates of terbium are shown in Table 2. Compounds (1) and (2) are available through commercial suppliers. Compound (3) is a novel fluorescent chelate based on the ligand imidotetraphenyldiphosphinic acid (5). Their relative light outputs in tritiated polystyrene are shown in Table 2.

The relative light outputs were determined using a standard luminometer with 2% w/v fluor in tritiated styrene at 100 µCi/ml. Polymerisation carried out at 100°C with t-butylperoxide initiator.



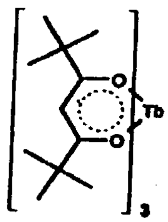
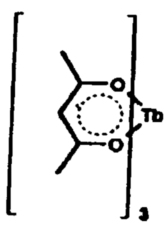
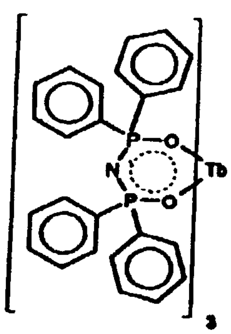
Imidotetraphenyldiphosphinic acid

(5)

EXAMPLE 10

Example 1 describes the compound ALP-1 which contains a Lewis base adduct in the form of diphenylphosphonimido triphenylphosphorane. This compound confers high solubility in styrene and high fluorescence efficiency on tris(2,2,6,6-tetramethyl-3,5-heptanedionato) terbium (III) when adducted. Therefore, work was undertaken to vary the functionality of this phosphorane compound to investigate structure/fluorescence efficiency relationships when adducted to terbium chelates. The relative light outputs were determined using a standard luminometer with 1 mmol/ml fluor in tritiated styrene

Table 2. Relative Light Output of Some Terbium 1,3-Diketonate Chelates

Chelate	Compound Number	Relative Light Output (Arbitrary units)
	(1)	25
	(2)	50
	(3)	10
ALP-1	(4)	100

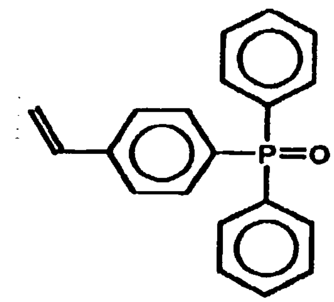
at 100 µCi/ml, polymerisation carried out at 100°C with t-butylperoxide initiator. The results are shown in Table 3. All the compounds shown in Table 3 were also incorporated in high radioactive concentration polystyrene, and showed the characteristic green emission of terbium fluorescence displayed by ALP-1.

EXAMPLE 11

A more general investigation of other Lewis base adducts was carried out. Adducts of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium (III) were prepared in situ during polymerisation. The relative light outputs were determined using a standard luminometer with chelate:Lewis base (1:1) at 1 mmol/ml in styrene at 100 µCi/ml. Polymerised at 100°C with t-butylperoxide initiator. The results are shown in Table 4.

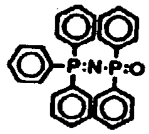
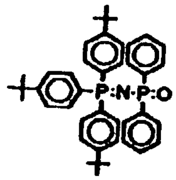
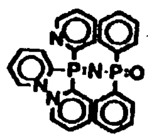
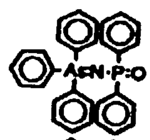
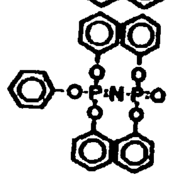
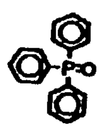
EXAMPLE 12

A polymerisable phosphine oxide, p-styryldiphenyl phosphine oxide (12) was prepared and its adduct with tris(2,2,6,6-tetramethyl-3,5-heptanedionato)terbium (III) prepared in situ as described. Results were obtained for various fluor loadings and were shown to be essentially the same (up to a fluor concentration of 5% w/v) as for triphenyl phosphine oxide.



(12)

Table 3. **Relative Light Outputs of Various Phosphorane Adducts of Tris (2,2,6,6-tetramethyl-3,5-heptanedionato)terbium (III)**

Phosphorane Adduct	Compound Number	Relative Light Output (Arbitrary units)
	(4)	100
	(6)	83
	(7)	64
	(8)	64
	(9)	50
	(10)	98
$(n\text{-}C_8H_{17})_3P{=}O$	(11)	82